Problem Set 2

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1)

1.a)

$$a = 0.11 \text{ nm} \qquad \kappa = 2.3 \times 10^3 \frac{N}{m} \tag{1}$$

$$E_{n,l} = \left(n + \frac{1}{2}\right)\hbar\sqrt{\frac{\kappa}{\mu}} + \frac{\hbar^2 l(l+1)}{2\mu a^2} \tag{2}$$

We can find the energies corresponding to the ground state $(n = 0, l = 0)$ and the states where one of the quantum numbers is nonzero.

$$\begin{aligned} E_{0,0} &= \frac{1}{2}\hbar\sqrt{\frac{\kappa}{\mu}} \\ E_{1,0} &= \frac{3}{2}\hbar\sqrt{\frac{\kappa}{\mu}} \\ E_{0,1} &= \frac{1}{2}\hbar\sqrt{\frac{\kappa}{\mu}} + \frac{\hbar^2}{\mu a^2} \end{aligned} \tag{3}$$

Now we can find the amount of energy required to bring the N_2 molecule to have energy stored in vibrations or rotation.

$$\begin{aligned} \Delta E_{\text{vib}} &= E_{1,0} - E_{0,0} \\ &= \hbar\sqrt{\frac{\kappa}{\mu}} \\ &= 4.69 \times 10^{-20} \quad \text{J} \end{aligned} \tag{4}$$

$$\begin{aligned} \Delta E_{\text{rot}} &= E_{0,1} - E_{0,0} \\ &= \frac{\hbar^2}{\mu a^2} \\ &= 7.9 \times 10^{-23} \quad \text{J} \end{aligned} \tag{5}$$

The amount of energy from the temperature can be found using Boltzman's constant.

$$\begin{aligned} E_T &= K_B T \\ &= 4.14 \times 10^{-21} \quad \text{J} \end{aligned} \tag{6}$$

As we can see, $\Delta E_{\text{rot}} < E_T < \Delta E_{\text{vib}}$ which means that the rotational energy storage is active and vibrational is not.

1.b)

We know that the molar heat capacity is $20.8\frac{\mathrm{J}}{\mathrm{mol\ K}}$, and we can find the ratio of this heat capacity to the gas constant (R) which will give us the coefficient to hopefully be $\frac{5}{2}$.

$$\frac{20.7}{8.134} \approx 2.5 \tag{7}$$

So yes!

2)

$$\kappa = 1860\frac{N}{m} \qquad a = 0.113\ \mathrm{nm} \tag{8}$$

$$E_{\text{photon}} = \hbar\sqrt{\frac{\kappa}{\mu}} \pm I\frac{\hbar^2}{\mu a^2} = \frac{hc}{\lambda} \tag{9}$$

Solve for λ:

$$\lambda = \frac{2\pi c}{\sqrt{\frac{\kappa}{\mu}} \pm I\frac{\hbar}{\mu a^2}} \tag{10}$$

Now we can plug in $I = -2, -1, 1, 2$ to get the possible wavelengths.

$$\begin{aligned} \lambda_{-2} &= 4.68\mu m \\ \lambda_{-1} &= 4.67\mu m \\ \lambda_{1} &= 4.65\mu m \\ \lambda_{2} &= 4.64\mu m \end{aligned} \tag{11}$$

3)

$$H = \frac{\hbar}{2}\begin{pmatrix} \omega_0 + \omega_1 & \omega_2 \\ \omega_2 & -\omega_0 - \omega_1 \end{pmatrix} \tag{12}$$

We want to calculate the following determinant to find the eigenvalues/vectors.

We leave out the $\frac{\hbar}{2}$ until the last step.

$$\begin{aligned} \begin{vmatrix} \omega_0 + \omega_1 - E & \omega_2 \\ \omega_2 & -\omega_0 - \omega_1 - E \end{vmatrix} &= 0 \\ (\omega_0 - E)(-\omega_0 - \omega_1 - E) - \omega_2^2 &= \\ -\omega_0^2 - \omega_2\omega_1 - \omega_0 E - \omega_1\omega_0 - \omega_1^2 - \omega_1 E + \omega_0 E + \omega_1 E - E^2 - \omega_2^2 &= \\ -\omega_0^2 - 2\omega_0\omega_1 + E^2 - \omega_2^2 - \omega_1^2 &= \\ E^2 &= \omega_0^2 + \omega_1^2 + \omega_2^2 + 2\omega_0\omega_1 \\ \implies E &= \frac{\hbar}{2}\left(\pm\sqrt{(\omega_0 + \omega_1)^2 + \omega_2^2}\right) \end{aligned} \tag{13}$$

So our diagonal Hamiltonian is:

$$\frac{\hbar}{2}\begin{pmatrix} \sqrt{(\omega_0+\omega_1)^2+\omega_2^2} & 0 \\ 0 & -\sqrt{(\omega_0+\omega_1)^2+\omega_2^2} \end{pmatrix} \tag{14}$$